Interpretation and Modelling of Thermodynamic Data Generated by ARC (Accelerating Rate Calorimeter)

Final Report

by

B.C.-Y. Lu, W.K. Chung and J.M. Yu

Department of Chemical Engineering, University of Ottawa

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OBJECTIVES OF WORK

The work of this contract is related to the research endeavours of CANMET for developing the technical knowledge necessary to improve existing hazard evaluation standards for explosives.

The Canadian explosives Research Laboratory of CANMET purchased in 1981 an accerating rate calorimeter (ARC) and used it for studying the thermal stability of commercial explosives.

The objectives of this contract as stated in the "Statement of Work" are as follows:

1) To interface the ARC with existing laboratory computer;
2) To develop the necessary software to use not only existing ARC equations but thermodynamic equations to interpret existing data (computer code with many subroutines);
3) To evaluate existing data using several potential thermodynamic equations (approaches) to provide best fit analysis.
4) To verify that, in fact, a thermodynamic approach is feasible and to establish the necessary guidelines for future development of a detailed thermodynamic model.

INTRODUCTION

This report describes the activities and results obtained for the study on "Interpretation and Modelling of thermodynamic Data Generated by ARC (Accelerating Rate Calorimeter) during the period from September, 1984 to March, 1985.

The work was carried out in accordance with the "Statement of Work" of the contract:

1) To interface the ARC using existing RS-232 port to either a T.I. business computer or Osborne Executive, so that data from the ARC can be stored on floppy disc for future retrieval and analysis.
2) To develop software for the computer that can read the stored data and analyse the data using the Arrhenius type equations used by the ARC. Part of the software necessary will be a graphics package to display the results on either the screen or X - Y plotter. The software should be sufficiently versatile, i.e. with adequate subroutines, to easily substitute thermodynamic equations to fulfill the following requirements.
3) To identify suitable thermodynamic approaches, incorporate the necessary equations into the software developed in (2) and evaluate existing data to provide a best fit analysis.
4) To correlate thermodynamic parameters determined in (3) with literature values to determine whether a thermodynamic approach is, in fact, feasible. To establish the necessary guidelines including mathematical description of transport phenomena, thermodynamic and equipment characteristics (heat transfer, heat capacity, et) for future development of a detailed thermodynamic model.

We have searched the literature concerning the use of ARC and the analysis of experimental data obtained from ARC, and reviewed possible models for treating

the ARC data. Monthly reports were duly made during the period as required. This report is the final report of work completed.

INTERFACING ARC WITH LABORATORY COMPUTER

An interface between the ARC and a Texas Instruments computer available in the laboratory was established, making it feasible to directly feed the data generated by the ARC to the computer's diskette.

In order to secure Fortran programming capability, the computer was upgraded by expanding its memory storage from 128 K to 256 K. A Fortran compiler was purchased and several test runs including the compiler were performed. The integrated system was found to be capable of serving the purpose of this study.

The modelling of thermodynamic data was performed through a computer package named ARC, written in Fortran language. The output of the package was devised so that all the information provided by the ARC experiments could be listed. A sample of the output listing is included in Appendix.

It may be mentioned that more than ten visits were made to CANMET for this phase of the study.

MODEL USED FOR CORRELATING ARC DATA

In order to study the thermal decomposition of explosives in terms of the ARC data, it is necessary to establish a thermokinetic model to describe the kinetic events of an explosive trigged by exposing it to a thermal source.

In this study, a generalized Arrhenius expression (1)

$$k = \alpha T^{j} e^{-E/RT} \qquad (1)$$

was adopted for correlating the data generated by ARC. In Eq. 1, k is the reaction constant, T refers to the absolute temperature, j is an empirical parameter, E is the activation energy and R is the universal gas constant.

The constant k is related to the change of concentration of reactant C with time t during the thermal decomposition of the explosive by means of Eq. 2,

$$\frac{dC}{dt} = - kC^{n} \tag{2}$$

The quantity "n" is the order of reaction. The application of Eq. 2 involves the assumption that for multiple or chain reactions of a single reactant, the overall kinetic event is considered to be equivalent to a single nth-order reaction.

To avoid the need of acquiring the value of C_o in the development, a pseudo reaction constant k* is defined,

$$k^* = k\ C_o^{n-1} \tag{3}$$

where the subscript "o" denotes the initial concentration of the explosive. Hence, the following relationship is obtained from Eq. 1:

$$\ln\left(\frac{k^*}{T^j}\right) = \ln\left(\alpha C_o^{n-1}\right) - \frac{E}{RT} = A^* - \frac{E}{RT} \tag{4}$$

Since ARC data are recorded in terms of the heat rate, a thermodynamic relation is required to correlate this quantity with temperature. With the assumption that at any given temperature T or time t, the concentration of the explosive can be approximately related to the temperature in the bomb of ARC,

$$C = \frac{T_f - T}{\Delta T_{AB}} C_o . \tag{5}$$

The fundamental equation relating the measurable thermal quantity T to the kinetic event can be obtained by differentiating Eq. 5 with respect to t and substituting the resulting expression into Eq.2 :

$$m_T = \frac{dT}{dt} = k \left(\frac{T_f - T}{\Delta T_{AB}}\right)^n \Delta T_{AB} \cdot C_o^{n-1} \tag{6}$$

In these equation, T_f is the final temperature when the reaction is completed, $\Delta T_{AB} = (T_f - T_o)$ is the temperature rise during the adiabatic reaction process, and T_o is the starting temperature for the thermal decomposition to occur without the support of any outside thermal source. The self-heat rate, m_T, is the experiment quantity measured by ARC.

Rearranging Eq. 6 yields

$$k^* = m_T / \left(\frac{T_f - T}{\Delta T_{AB}}\right)^n \cdot \Delta T_{AB} \tag{7}$$

Eq. 7 makes it feasible to calculate k* using the experimental values, m_T, T_f and ΔT_{AB} generated from ARC at a given temperature T and a reaction order "n". Subsequently the calculated k* values are used to determine the quantities A* and E of Eq. 4 by means of a least-squares fit.

In this study, the quantities j and n were considered as adjustable parameters, with their values determined from the best representation of the ARC data. A software computer package in Fortran language was developed for the Texas

Instruments computer. This package is capable of executing routine correlation of the ARC data as soon as they are collected. The input and output specifications of the package are well documented as shown in the Appendix section. All the subroutines required for evaluating the parameters of Eq. 1 are included in the package.

In addition, the package is capable of calculating heat of reaction, ΔH_r, provided the heat capacity of the explosive at constant volume, C_v, and the thermal inertia, Φ, are known. Namely,

$$\Delta H_r = M\, C_v\, \Delta T_{AB}\, \Phi \qquad (8)$$

The quantity M is the mass of the explosive sample placed in the bomb.

CORRELATION OF ARC DATA

The heat rate data for ammonium nitrate (AN), determined from ARC at CANMET, were used to test the validity of the selected model (Eq. 4). The quantities j and n were adjusted to minimize the average deviation between the calculated and the experimental values by means of a least-squares fit of the ARC data by means of Eq. 4. The average absolute percentage deviation was found to be less than 0.5% with n = 0.0047 and j = 4.45. The maximum deviation of 1.5% was observed at low temperatures. The calculated activation energy from Eq. 4 is 53.2 Kcal/mole.

Subsequent tests of the model by means of the ARC data determine at CANMET for different explosives also revealed very small values of n. For this reason, the order of reaction "n" was set to be zero in subsequent calculations.

A total of 3414 ARC data points for 49 samples were correlated with n = 0,

but using this quantity j of Eq. 4 as the adjustable parameter. A complete list of the explosives together with the correlated results are presented in Table 1. In addition, the calculated activation energies are compared with the values obtained from the build-in ARC software program using the original Arrhenius law (j = 0, activation energy = E_o) and those reported in the literature (E_ℓ) using thermal decomposition data from other methods. The E_ℓ values were generally calculated using the Arrhenius law. These comparisons are also presented in Table 1.

Deviation in k*

The results reported in Table 1 indicate that the data generated by ARC at CANMET can be represented by Eq. 4 with average absolute percentage deviations in k* around 1.5%.

Comparison of activation energies

As far as the comparison of activation energies is concerned, the calculated E values using the proposed model are usually lower than the E_o values by about 10%, but the difference between E and Eℓ values may be larger. For TNT (see Run 168), value of E (78.4 Kcal/mole) is in good agreement with E_o (85.5 Kcal/mole), but is quite different from the Eℓ value (34.4 Kcal/mole).

On the other hand, the agreement between E and Eℓ values are considered acceptable for ammonium nitrate, nitrocellulose, ethyl nitrate and PETN.

Values of j

It is of interest to note that for most explosives tested, the values of j are close to a value of 4.

CONCLUSIONS AND RECOMMENDATIONS

The model was found to be adequate for describing thermokinetic event for relatively simple thermal decompositions. The assumption of zeroth order of reaction was found to be suitable for correlating the data for the samples tested and the values of j were found to be close to a value of 4.

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Table 1 Summary of correlation results and comparison of activation energy values

Run no.	Data Point	Explosive	E Kcal/ mole	j	k*, %	E_o Kcal/ mole	E ℓ Kcal/ mole	Ref
198	89	AN + 0.1% Mg st	52.0	4.89	1.59	-		
197	106	AN + 0.1% Ca st	38.2	4.89	1.46	-		
196	103	AN + 0.1% Ca st	40.8	4.86	1.32	56.1		
191	73	AN + 2% Mg st	70.4	4.75	1.69	-		
189	117	Ammonium Nitrate	37.5	4.80	1.44	55.1	31.4,38.5 36.5,39.0	(2)
188	60	AN + 2% Mg st	74.4	4.43	1.03	94.3		
194	100	AN + 0.1 % Mg st	37.8	1.33	4.13	-		
190	83	AN + 2% Mg st	80.0	-2.85	11.3	102.8		
187	64	AN + 2% Ca st	77.6	4.16	1.33	94.3		
186	80	Ammonia Nitrate	50.0	4.83	0.67	61.1		
185	104	"	40.8	4.85	1.69	60.9		
184	114	"	38.6	4.79	0.98	55.8		
134	88	AN - C prill	45.2	2.27	1.46	-		
132	122	"	33.7	4.17	1.79	-		
130	75	"	50.0	4.51	0.65	-		
126	76	AN + dodecane	57.6	4.87	1.39	-		
125	67	AN + dodecane	62.0	3.03	1.87	-		
124	87	AN (aeroprill)	55.6	4.80	2.00	-		
118	72	AN + dodecane	52.4	4.19	3.50	-		
117	107	"	41.2	3.93	0.82	-		
116	67	"	64.8	4.66	5.93	-		
115	40	"	102.0	3.11	1.25	-		

Table 1 (Cont'd)

Run no.	Data Point	Explosive	E Kcal/ mole	j	k*, %	E_o Kcal/ mole	E_ℓ Kcal/ mole	Ref
114	82	AN + dodecane	56.4	4.72	1.85	-		
99	84	AN granular	49.6	4.73	1.46	-		
95	88	AN aeroprill	53.6	4.75	1.76	-		
93	74	"	62.8	0.15	3.69	-		
92	74	"	47.6	4.79	1.12	-		
90	68	"	60.0	4.69	2.37	-		
86	52	AN granular	80.4	3.43	2.50	-		
85	68	"	59.2	4.27	3.40	-		
84	73	"	48.0	0.61	13.3	-		
83	59	"	64.0	4.73	1.81	-		
81	32	"	124.8	1.83	0.66	-		
80	19	"	205.6	4.11	0.26	-		
182	49	TNT	84.0	4.05	2.39	-	34.4	(3)
168	43	TNT	78.4	2.60	1.93	84.5	34.4	(3)
59	34	Nitro cellulose	66.0	4.35	0.47	-	46.2	(4)
46	36	"	68.0	3.10	0.62	-	46.2	(4)

Table 1 (Cont'd)

Run no.	Data Point	Explosive	E Kcal/ mole	j	k*, %	E_o Kcal/ mole	Eℓ Kcal/ mole	Ref
229	35	Ethyl nitrate	44.8	2.84	6.24	-	39.90	(2)
227	33	Ethyl nitrate	48.8	2.89	4.57	-	39.90	(2)
181	54	PETN	58.0	2.90	1.17	71.0	47.0	(5) (6)
172	59	PETN	61.2	2.78	3.93	63.3	47.0	(5) (6)
222	82	ANT + 10% Z_n	58.0	2.68	7.55	66.7		
219	37	AN + 5% C_a	108.8	1.40	1.59	132.7		
211	83	AN + 10% Fe	46.8	4,72	0.28	64.2		
199	81	AN + 10% Aℓ	44.8	4.43	2.51	57.1		
133	11	AMEX II (CIL) (Dupont)	75.2	-1.38	1.34			
129	28	ANFO, Nilite FR	57.2	-1.39	5.44			
127	82	"	41.2	-2.49	8.77			

APPENDIX

COMPUTER PROGRAMS

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Program Listing	14 - 28
Output Listing	29 - 34

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

C ***************************************************************************     AR
C                                                                                  AR
C      PROGRAM NAME = RATE2                                                        AR
C      PURPOSE : TO DEVELOP THERMOKINETIC MODEL FOR THERMAL ANALYSIS               AR
C      DATE = OCT 1984                                                             AR
C      PROGRAMMING LANGUAGE : FORTRAN                                              AR
C      TEST 1                                                                      AR
C ***************************************************************************     AR
C                                                                                  AR
C      ***************************************************************           AR
C      *                                                             *           AR
C      *                  MAIN    PROGRAM                            *           AR
C      *                                                             *           AR
C      ***************************************************************           AR
C                                                                                  AR
       DIMENSION TITLE(80),NOUT(40),OUT(40,6)                                      AR
       COMMON /BK1/ T(200),RT(200),RMT(200),PP(200),DTAB,TF,ND                     AR
       COMMON /BK2/ FOB,RJ,RNS                                                     AR
       COMMON /BK3/ RKS(200),RE,RA                                                 AR
       COMMON /BK4/ COEF(5),SDY,EDYAV,SDYAV,XMEDY,MP1                              AR
       COMMON /BK5/ KCH                                                            AR
       DATA RR/'R'/                                                                AR
       DATA RU/'U'/                                                                AR
       DATA RN/'N'/                                                                AR
       DATA SAS/'S'/                                                               AR
       DATA SAA/'A'/                                                               AR
       DATA SAM/'M'/                                                               AR
       DATA BOB/'B'/                                                               AR
       DATA BOO/'O'/                                                               AR
       DATA BOT/'T'/                                                               AR
       DATA BOM/'M'/                                                               AR
       DATA EXE/'E'/                                                               AR
       DATA EXX/'X'/                                                               AR
       DATA EXO/'O'/                                                               AR
C      RMT = TEMPERATURE RATE, DEGREE K/ MIN.                                      AR
C      RKS = PSEUDO RATE CONSTANT                                                  AR
C      RE  = ACTIVATION ENERGY, KCAL/MOLE                                          AR
C      RA  = FREQUENT FACTOR, 1/MIN.                                               AR
C      RN  = REACTION ORDER                                                        AR
C      RJ  = TEMPERATURE FACTOR                                                    AR
C      RT  = REACTION TIME, MIN.                                                   AR
C      T   = TEMPERATURE, DEGREE K                                                 AR
C      PP  = PRESSURE,PSIA                                                         AR
C      TF  = FINAL TEMPERATURE, DEGREE K                                           AR
C      T0  = T(1), INITIAL TEMPERATURE,DEGREE K                                    AR
C      DTAB = OVERALL TEMPERATURE DIFFERENCE (TF- T0), DEGREE C                    AR
C      IGN = 1  THE DATA AFTER THIS POINT ARE FOR EXPLOSION OR BEGINNING           AR
C               OF FLUCTUATING DATA TO BE DISCARDED                                AR
C      IGN = 2  THE END OF THE EXPLOSIN DATA OR FLUCTUATING DATA                   AR
C      IGN = 3  THE END OF THE EXOTHERM DATA                                       AR
C      NBT = 1   BOMB TYPE TI,CVB= 0.14, = 2 BOMB TYPE IS S.S.,CVB = 0.12,         AR
C          = 3  BOMB TYPE IS HASTELLORY C. CVB = 0.10 CAL/G,C                      AR
C      SM = SAMPLE MASS, CVS = 0.5 CAL/G,C ( AVERAGE ), BM = BOMB MASS             AR
C      CVS = HEAT CAPACITY AT CONSTANT VOL. OF SAMPLE                              AR
C      CVB = HEAT CAPACITY AT CONSTANT VOL. OF BOMB                                AR
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR S

C       DH = HEAT OF REACTION
C       XRMT = MAX. SELF-HEAT RATE
C       TEMXR = TEMP.(K) AT MAX. RATE ,TM
C       TIMEXR = TIME (MINUTE) TO MAX. RATE,TIMEM
C       PREXR = PRESSURE (PSIA) AT TM
C       T(1) = INITIAL TEMP. (K),TI
C       PP(1)= INITIAL PRESSURE (PSIA) AT TI
C       RMT(1) = RATE AT INITIAL TEMP.
        III = 0
C       DTA8PH = DTA8*PHI
C       P1RATE = PRESSURE RATE AT T(1),PSIA/MIN
C       PMRATE = PRESSURE AT MAX. RATE, PSIA/MIN
C       PREXR1 = PRESSURE (PSIA) BEFORE THE MAX. RATE
C       RTS1   = TIME BEFORE THE MAX. RATE
C
C       INPUR RAW DATA FROM ARC
C
 1001 READ(5,500,END=999) (TITLE(I),I=1,80)
        XRMT = -10.0
        NMAX = 1
  500 FORMAT(80A1)
        IF (TITLE(9) .EQ. RR .AND. TITLE(10).EQ. RU ) GO TO 1000
        IF (TITLE(5) .EQ. SAS .AND. TITLE(6) .EQ. SAA) GO TO 2000
        IF (TITLE(5) .EQ. BOB .AND. TITLE(6) .EQ. BOO .AND. TITLE(10)
       * .EQ. BOM) GO TO 3000
        IF (TITLE(5) .EQ. BOB .AND. TITLE(8) .EQ. BOO .AND. TITLE(10)
       * .EQ. BOT) GO TO 4000
        IF (TITLE(5) .EQ. EXE .AND. TITLE(6) .EQ. EXX .AND. TITLE(7)
       * .EQ. EXO) GO TO 5000
        GO TO 1001
 1000 CONTINUE
        READ(5,501) NDUMMY,NRUN
  501 FORMAT(2I9)
        WRITE(6,600) (TITLE(I),I=1,25),NRUN
  600 FORMAT(2X,25A1,'  =  ',I4)
        GO TO 1001
 2000 CONTINUE
        READ(5,502) DUMMY,SM
  502 FORMAT(2F10.5)
        WRITE(6,620) (TITLE(I),I=1,25),SM
  620 FORMAT(2X,25A1,'  =  ',F10.5,' GRAM'/)
        GO TO 1001
 3000 CONTINUE
        READ(5,502) DUMMY,BM
        WRITE(6,630) (TITLE(I),I=1,25),BM
  630 FORMAT(2X,25A1,'  =  ',F10.5,' GRAM'/)
        GO TO 1001
 4000 CONTINUE
        READ(5,501) NDUMMY,NBT
        WRITE(6,600) (TITLE(I),I=1,25),NBT
        GO TO (101,102,103,103,103),NBT
  101 CVB = 0.14
        GO TO 104
  102 CVB = 0.12
        GO TO  104
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

  103 CVB = 0.10                                                          AR
      GO TO 104                                                           AR
  104 CONTINUE                                                            AR
      CVS = 0.5                                                           AR
      PHI = 1. + CVB*BM/(CVS*SM)                                          AR
      READ(5,500) (TITLE(I) ,I=1,25)                                      AR
      READ(5,501) NDUMMY,NDATAT                                           AR
      DO 699 J = 1,13                                                     AR
      READ(5,500) (TITLE(I),I=1,25)                                       AR
      READ(5,502) DUMMY,XXX                                               AR
      WRITE(6,660) (TITLE(I),I=5,25),XXX                                  AR
  660 FORMAT(2X,21A1,' = ',F10.4)                                         AR
  699 CONTINUE                                                            AR
      GO TO 1001                                                          AR
 5000 CONTINUE                                                            AR
      WRITE(6,650) (TITLE(I),I=1,25)                                      AR
      READ(5,500) (TITLE(I),I=1,25)                                       AR
      WRITE(6,650) (TITLE(I),I=1,25)                                      AR
  650 FORMAT(2X,25A1)                                                     AR
      DO 700 J = 1,5                                                      AR
      READ(5,500) (TITLE(I),I=1,25)                                       AR
  700 CONTINUE                                                            AR
      II = 0                                                              AR
      RJ = 0.0                                                            AR
      RTS = 0.0                                                           AR
      P = 0.0                                                             AR
      I = 1                                                               AR
11    CONTINUE                                                            AR
      P1 = P                                                              AR
      RTS1 = RTS                                                          AR
      READ(5,2) RTS,TS,RMTS,IGN                                           AR
      READ(5,2) XDUMMY, P,XDUMMY,IGN                                      AR
2     FORMAT(3F7.2,I4)                                                    AR
      IF(RTS.LT.0.0 .OR. IGN .EQ. 3) GO TO 15                             AR
      IGN1 = IGN                                                          AR
      T(I) = TS                                                           AR
      T(I) = T(I) + 273.15                                                AR
      RT(I) = RTS                                                         AR
      RMT(I) = RMTS                                                       AR
      PP(I) = P                                                           AR
      IF(XRMT .LT. RMT(I)) GO TO 410                                      AR
  420 CONTINUE                                                            AR
       I1 = I - 1                                                         AR
      IF (IGN .EQ. 1) GO TO 220                                           AR
      IF (IGN .EQ. 2) GO TO 151                                           AR
      IF (II .EQ. 1) GO TO 11                                             AR
      IF ( I .EQ. 1) GO TO 402                                            AR
      IF (RTS .LT. RT(I1).OR. TS .LT.(T(I1)-273.15)) WRITE(6,400) RTS,TS AR
  400 FORMAT(2X,'INPUT ERROR',F10.5)                                      AR
  402 I = I + 1                                                           AR
      GO TO 11                                                            AR
  410 XRMT = RMT(I)                                                       AR
      TEMXR = T(I)                                                        AR
      TIMEXR = RT(I) - RT(1)                                              AR
      PREXR = PP(I)                                                       AR
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SY

      NMAX = I
      PREXR1 = P1
      TEXR1 = RTS1
      GO TO 420
  220 II = 1
      GO TO 11
  151 II = 0
      GO TO 11
   15 CONTINUE
      ND = I-1
      TF = T(I)
      IF (IGN1 .EQ. 0 )   GO TO 1001
      DTAB = TF     - T(1)
      WRITE(6,681) T(1),RMT(1),PP(1),XRMT,TEMXR,TIMEXR,PREXR,TF
  681 FORMAT(2X,'INITIAL TEMP.(K),TI                    = ',F12.3/
     *       2X,'RATE AT INITIAL TEMP.                  = ',F12.3/
     *       2X,'PRESSURE(PSIA) AT INITIAL TEMP.        = ',F12.3/
     *       2X,'MAX. SELF-HEAT RATE                    = ',F12.3/
     *       2X,'TEMP.(K) AT MAX. SELF-HEAT RATE        = ',F12.3/
     *       2X,'TIME (MINUTE) TO MAX. RATE             = ',F12.3/
     *       2X,'PRESSURE(PSIA) AT MAX. RATE            = ',F12.3/
     *       2X,'FINAL TEMP.(K)                         = ',F12.3)
      WRITE(6,601) DTAB,TF,PHI
  601 FORMAT(2X,'TEMPERATURE RISE,K                     = ',F12.3/
     *       2X,'MAXIMUN TEMPERATURE,K                  = ',F12.3/
     *       2X,'BOMB CORRECTION FACTOR,(PHI)           = ',F12.3)
      DH = SM * PHI*CVS*DTAB
      DTABPH = DTAB*PHI
      P1RATE = (PP(2)-PP(1))/(RT(2)-RT(1))
      PMRATE = (PREXR      -PREXR1   )/(TIMEXR+RT(1) -TEXR1)
C     WRITE(6,685) NMAX,PP(NMAX),RT(NMAX),PREXR1,TEXR1
  685 FORMAT(5X,'TEST',I5,4F12.3)
      WRITE(6,682) DTAB,DTABPH,P1RATE,PMRATE,DH,CVS,CVB
  682 FORMAT(2X,'ADIABATIC RISE                         = ',F12.3/
     *       2X,'ADIABATIC RISE * PHI                   = ',F12.3/
     *       2X,'PRESSURE RATE AT INITIAL TEMP.         = ',F12.3/
     *       2X,'PRESSURE RATE AT MAX. RATE(PSIA/M)     = ',F12.3/
     *       2X,'HEAT OF REACTION                       = ',F12.3/
     *       2X,'HEAT CAP. AT CONS. VOL. OF SAMPLE      = ',F12.3/
     *       2X,'HEAT CAP. AT CONSTANT VOL.OF BOMB      = ',F12.3)
C     ASSUMING REACTION ORDER
C     RANGE COP < DOP
      COP = -3.0
      DOP =  5.0
      TOL = 1.E-05
C     RN = 0.0
      KCH = 0
      OR = BMIN(COP,DOP,TOL)
      KCH = 1
      RJ = OR
      RN = RNS
C     CALL DEV(RN)
      WRITE(6,670)
  670 FORMAT(//2X,' YEXP(I) = ITH EXPERIMENTAL VALUE OF LN(RKS/T**RJ)'/
     *         2X,' YC(I) = ITH CALCULATED VALUE OF LN(RKS/T**RJ) '
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

     *          ,'USING FITTED PN,RJ,RE AND RA, = RA + RE/(R*T)'/          AR
     *         2X,' R = GAS CONSTANT, 1.987'/                              AR
     *         2X,' RN = REACTION ORDER'/                                  AR
     *         2X,' RJ = TEMPERATURE FACTOR'/                              AR
     *         2X,' RE = ACTIVATION ENERGY, CAL/MOLE'/                     AR
     *         2X,' RA = FREQUENCY FACTOR'/                                AR
     *         2X,' SDY = SUMMATION OF (YC(I) - YEXP(I)) FOR ALL I'/       AR
     *         2X,' EDYAV = AVERAGE ABS((YC(I)-YEXP(I))/YEXP(I))*100'/     AR
     *         2X,' SDYAV = AVERAGE ABS(YC(I)-YEXP(I))'/                   AR
     *         2X,' XMEDY = MAX. ABS((YC(I)-YEXP(I))/YEXP(I))*100'/        AR
     *         2X,' DH = HEAT OF REACTION, CAL.')                          AR
      WRITE(6,10) SDY,EDYAV,SDYAV,XMEDY,DH                                 AR
10    FORMAT(//2X,'SDY=',F10.2,2X,'EDYAV=',F10.3,2X,'SDYAV=',F10.3,2X,     AR
     1       'XMEDY=',F10.3,' DH = ',E12.5//)                              AR
      WRITE(6,5) ND,RE,RA,RN,RJ                                            AR
C    5 FORMAT(//2X,'ND= ',I5,2X,'RE=',F10.3,                               AR
C     12X,'RA=',F10.3,2X,'RN=',F10.6,2X,                                   AR
C     1 'RJ=',F10.6//)                                                     AR
     5 FORMAT(//2X,'NUMBER OF DATA POINTS = ',I5/                          AR
     *2X,'ACTIVATION ENERGY      = ',F10.3,' CAL/MOLE'/                    AR
     *2X,'FREQUENCY FACTOR       = ',F10.3/                                AR
     *2X,'REACTION ORDER         = ',F10.3/                                AR
     *2X,'TEMPERATURE FACTOR     = ',F10.3/)                               AR
      WRITE(6,710)                                                         AR
  710 FORMAT(2X,'DATA POINT NO.',2X,'TEMPERATURE',2X,'    TIME    ',2X,     AR
     *' HEAT RATE',2X,' PRESSURE')                                         AR
      DO 21 K = 1,ND                                                       AR
      WRITE(6,3) K,T(K),RT(K),RMT(K),PP(K)                                 AR
3     FORMAT(2X,I8,5X,F11.3,5X,F8.2,2X,F10.4,2X,F10.3)                     AR
21    CONTINUE                                                             AR
      IF(KCH.EQ.1) CALL DEV(RN)                                            AR
      III = III + 1                                                        AR
      NOUT(III) = ND                                                       AR
      OUT(III,1) = RE                                                      AR
      OUT(III,2) = RA                                                      AR
      OUT(III,3) = RN                                                      AR
      OUT(III,4) = RJ                                                      AR
      OUT(III,5) = XMEDY                                                   AR
      OUT(III,6) = DH                                                      AR
      GO TO 1001                                                           AR
  999 CONTINUE                                                             AR
      WRITE(6,611)                                                         AR
  611 FORMAT(5X,'ND',7X,'RE', 6X,'RA', 4X,'RN', 7X,'RJ', 5X,'XMEDY',3X,    AR
     *'DH')                                                                AR
      DO 155 K = 1, III                                                    AR
  155 WRITE(6,610) NOUT(K),(OUT(K,I),I=1,6)                                AR
  610 FORMAT(2X,I5,F12.3,F7.3,F5.2,F10.5,F8.2,F8.2)                        AR
      RETURN                                                               AR
      END                                                                  AR
C     ***************************************************************    AR
C     *                                                             *    AR
C     *              EVALUATION OF THERMOKINETIC MODEL              *    AR
C     *                                                             *    AR
C     ***************************************************************    AR
      SUBROUTINE DEV(RN)                                                   AR
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR S

      COMMON /BK1/ T(200),RT(200),RMT(200),PP(200),DTAB,TF,ND
      COMMON /BK2/ FOB,RJ,RNS
      COMMON /BK3/ RKS(200),RE,RA
      COMMON /BK4/ COEF(5),SDY,EDYAV,SDYAV,XMEDY,MP1
      COMMON /BK5/ KCH
      DIMENSION XK(200),YK(200),YC(200),DY(200),EDY(200)
      R = 1.987

C
C
C
      DO 21 I = 1,ND
C     WRITE(6,15) TF,T(I),DTAB,RMT(I),RKS(I),RN ,I
      RKS(I) = RMT(I)*(DTAB/(TF-T(I)))**RN/DTAB
      ARG = RKS(I)/T(I)**RJ
C     WRITE(6,15) TF,T(I),DTAB,RMT(I),RKS(I),ARG,I
      YK(I) = ALOG(ARG)
 15   FORMAT(2X,6E12.4,2X,I5)
      XK(I) = 1./T(I)
 21   CONTINUE
C
C     DEFINE LEAST SQUARE FIT - ORDER
C
      M = 1
      CALL CURM(XK,YK,M,YC,DY,EDY)
      RA = COEF(1)
      RE =-COEF(2)
      RE = RE*R
C     IF(KCH.EQ.0) GO TO 10
      AVY = 0.0
      AVP = 0.0
      IF (KCH .GT. 0) WRITE(6,20)
   20 FORMAT(2X,' T IS TEMPERATURE'/
     *       2X,' YKT = YKS'/
     *       2X,' YCT = CALCULATED VALUE OF YKS FROM FITTED COEFF',
     *          'ICIENTS, THESE ARE RJ,RN',                       /
     *       2X,'          FREQUENCY FACTOR AND ACTIVATION ENERGY'/
     *       2X,' RJ IS THETEMPERATURE FACTOR'/
     *       2X,' RN IS THE REACTION ORDER'/
     *       2X,' DYT = YCT - YKT'/
     *       2X,' EDYT = DYT/YKT*100%'/
     *       2X,' WHERE RKS = RMT*(DTAB/(TF-T))**RJ/DTAB'/
     *       2X,'          RMT IS THE TEMP RATE IN DEG. C/MIN.'/
     *       2X,'          TF  IS THE FINAL (MAXIMUM) TEMPERATURE IN ',
     *          'DEGREE K'/
     *       2X,'          T IS THE TEMPERATURE IN DEGREE K'/
     *       2X,'          DTAB = TF - INITIAL TEMPERATURE '/
     *       2X '                 = TEMPERATURE RISE IN DEGREE K')
      IF(KCH.GT.0) WRITE(6,19)
   19 FORMAT(2X,'DATA NO.',8X,'T',14X,'YKT',12X,'YCT',12X,'DYT',12X,
     *'EDYT')
      DO 23 K = 1,ND
C     IF(KCH.GT.0) WRITE(6,8) XK(K),YK(K),YC(K),DY(K),EDY(K),K
 8    FORMAT(2X,'F=',5F15.4,2X,I5)
      YKT = EXP(YK(K))*T(K)**RJ
```

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FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

      YCT = EXP(YC(K))*T(K)**RJ                                          AR
      DYT = YCT-YKT                                                      AR
      EDYT = DYT/YKT*100.                                                AR
      AVY = AVY+ABS(DYT)                                                 AR
      AVP = AVP+ABS(EDYT)                                                AR
      IF(KCH.GT.0) WRITE(6,18) K,T(K),YKT,YCT,DYT,EDYT                   AR
 18   FORMAT(2X,I5  ,5F15.4)                                             AR
 23   CONTINUE                                                           AR
      AVY = AVY/ND                                                       AR
      AVP = AVP/ND                                                       AR
C     IF(KCH.GT.0) WRITE(6,12) ND,AVY,AVP                                AR
  12  FORMAT(2X,'A=',2X,I5,'AVY,AVP=',2F10.5)                            AR
C                                                                        AR
C                                                                        AR
 10   CONTINUE                                                           AR
C     FOB = SDY                                                          AR
      FOB = AVP                                                          AR
      RETURN                                                             AR
      END                                                                AR
C     ************************************************************       AR
C     *                                                          *       AR
C     *                CURVE FIT                                 *       AR
C     *                                                          *       AR
C     ************************************************************       AR
C ****************************************************************       AR
C                                                                        AR
C       THIS PROGRAM IS TO FIT PSUEDO KINETIC CONSTANT WITH 1/T          AR
C                                                                        AR
C ****************************************************************       AR
      SUBROUTINE CURM (XK,YK,M,YC,DY,EDY)                                AR
      COMMON /BK1/ T(200),RT(200),RMT(200),PP(200),DTAB,TF,ND            AR
      COMMON /BK2/ FOB,RJ,RNS                                            AR
      COMMON /BK3/ RKS(200),RE,RA                                        AR
      COMMON /BK4/ COEF(5),SDY,EDYAV,SDYAV,XMEDY,MP1                     AR
      DIMENSION A(200,5),B(200,5),X(200),Y(200,1),C(200,5),YC(200),      AR
     1DY(200),EDY(200),WW(200)                                           AR
      DIMENSION XK(200),YK(200)                                          AR
      L = 1                                                              AR
C     M = 3                                                              AR
      N = ND                                                             AR
      DO 11 I = 1,N                                                      AR
      WW(I) = 1.                                                         AR
      X(I) = XK(I)                                                       AR
  74  CONTINUE                                                           AR
      Y(I,1) = YK(I)                                                     AR
C ****************************************                               AR
C      WRITE (6, 300) X(I), (Y(I,J), J = 1, L),WW(I)                     AR
  300 FORMAT (1H0, 3E14.7)                                               AR
   11 CONTINUE                                                           AR
      DO 30 I = 1, N                                                     AR
   30 C(I, 1) = 1.0                                                      AR
      MP1 = M+1                                                          AR
      DO 35 J =2, MP1                                                    AR
      DO 35 I = 1, N                                                     AR
   35 C(I,J) = C(I, J-1)*X(I)                                            AR
```

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FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR S

      DO 43 I = 1, MP1
      DO 40 J = 1, MP1
      A(I,J) =0.
      DO 40 K =1, N
   40 A(I,J) = A(I,J) + C(K,I)*C(K,J) *WW(K)
      DO 45 J = 1, L
      DO 45 I =1, MP1
      B(I,J) = 0.
      DO 45 K = 1, N
   45 B(I,J) = B(I,J) + C(K,I)*Y(K,J) *WW(K)
C ***************************************************************
C *
      CALL CHAP8(A, MP1, B, L, DET)
C *
C ***************************************************************
C     WRITE(6, 111)
  111 FORMAT (1H0, '-----------------------------------------')
C     WRITE (6, 301) N
  301 FORMAT(1H ,' THE NUMBER OF GIVEN DATA POINTS=', I3)
C     WRITE (6, 302) M
  302 FORMAT(1H , ' THE DEGREE OF POLYNOMIAL=',I3)
      DO 50 J = 1, L
      DO 50 I = 1, MP1
      II = I - 1
C     WRITE (6, 303) II, B(I,J)
      COEF(I) = B(I,J)
  303 FORMAT(1H0, I3,'   DEGREE COEFFICIENT= ', E14.7)
   50 CONTINUE
      SEDY = 0.
      SDY = 0.0
      XMEDY = 0.
      DO 70 J = 1, N
      YC(J) = 0.
      DO 60 IL = 1, L
      DO 60 I = 1, MP1
      II = I - 1
      YC(J) = YC(J) + B(I, IL)*X(J)**II
   60 CONTINUE
      DY(J) = YC(J) - Y(J,1)
      EDY(J) = 0.0
      IF(ABS(Y(J,1)).GE. 0.00001)
     * EDY(J) = (DY(J)/Y(J,1))*100.
       IF ( XMEDY .LT. ABS(EDY(J))) XMEDY = ABS(EDY(J))
      SEDY = SEDY + ABS(EDY(J))
      SDY = SDY + ABS(DY(J))
C     WRITE (6, 304) J, YC(J),J,DY(J) ,J, EDY(J)
C ********** CHANGE ************************************
   70 CONTINUE
C ********** CHANGE ************************************
  304 FORMAT(1H0,'  YC(',I2,')=',E14.6, '  DY(',I2,')=',E14.6,
     1'  EDY(',I2,')=',E14.6, '%')
      EDYAV =  SEDY/N
      SDYAV = SDY/N
C     WRITE (6,305) SDY, EDYAV,SDYAV
  305 FORMAT(1H0,' SUM OF DY=',E14.6, '  AVE. D.Y.=',E14.6, '%,  AVE. D.
```

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FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SY:

     1Y.=',E14.6)                                                          AF
C      WRITE ( 6, 308) XMEDY                                              AF
  308 FORMAT (1H0,' MAX. DEVIATION = ', E14.6)                            AF
C      WRITE(6,516) (COEF(I),I = 1,MP1)                                   AF
  516 FORMAT(1H ,4E14.6)                                                  AF
      RETURN                                                              AF
      END                                                                 AF
C ***************************************************************       AF
C                                                                         AF
C              SUPPORTING ROUTINE                                         AF
C                                                                         AF
C ***************************************************************       AF
      SUBROUTINE CHAP8 (A,N,B,M,DET)                                      AF
      DIMENSION A(200,5),B(200,5),IPVOT(40),INDEX(40,2),PIVOT(40)         AF
      COMMON IPVOT, INDEX, PIVOT                                          AF
      EQUIVALENCE (IROW, JROW), (ICOL, JCOL)                              AF
C   FOLLOWING 3 STATEMENTS FOR INITIALIZATION                             AF
   57 DET = 1.                                                            AF
      DO 17 J = 1, N                                                      AF
   17 IPVOT(J) = 0                                                        AF
      DO 135 I = 1, N                                                     AF
C      FOLLOWING 12 STATEMENTS FOR SEARCH FOR PIVOT ELEMENT               AR
      T = 0.                                                              AR
      DO 9 J = 1, N                                                       AR
      IF (IPVOT(J) - 1) 13, 9, 13                                         AR
   13 DO 23 K = 1, N                                                      AR
        IF (IPVOT(K) -1) 43, 23, 81                                       AR
   43 IF(ABS(T) - ABS(A(J,K))) 83, 23, 23                                 AR
   83 IROW = J                                                            AR
      ICOL = K                                                            AR
      T = A(J, K)                                                         AR
   23 CONTINUE                                                            AR
    9 CONTINUE                                                            AR
      IPVOT(ICOL) = IPVOT(ICOL) + 1                                       AR
C    FOLLOWING 15 STATEMENT TO PUT PIVOT ELEMENT ON DIAGONAL              AR
      IF (IROW - ICOL) 73, 109, 73                                        AR
   73 DET = - DET                                                         AR
      DO 12 L = 1, N                                                      AR
      T = A(IROW, L)                                                      AR
      A(IROW, L) = A(ICOL, L)                                             AR
   12 A(ICOL, L) = T                                                      AR
      IF(M) 109, 109, 33                                                  AR
   33 DO 2 L = 1, M                                                       AR
      B(IROW, L) = B(ICOL, L)                                             AR
      T = B(IROW, L)                                                      AR
    2 B(ICOL, L) = T                                                      AR
  109 INDEX(I,1) = IROW                                                   AR
      INDEX(I,2) = ICOL                                                   AR
      PIVOT(I) = A(ICOL, ICOL)                                            AR
      DET = DET*PIVOT(I)                                                  AR
C      FOLLOWING 6 STATEMENTS TO DIVIDE PIVOT ROW BY PIVOT ELEMENT        AR
      A(ICOL, ICOL) = 1.                                                  AR
      DO 205 L = 1, N                                                     AR
  205 A(ICOL, L) = A(ICOL, L)/PIVOT(I)                                    AR
      IF (M) 347, 347, 66                                                 AR
```

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FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR S

    68 DO 52 L = 1, M
    52 B(ICOL, L) = B(ICOL, L)/PIVOT(I)
C     FOLLOWING 10 STATEMENTS TO REDUCE NON-PIVOT ROWS
   347 DO 135 LI = 1, N
       IF(LI - ICOL) 21, 135, 21
    21 T = A(LI, ICOL)
       A(LI, ICOL) = 0.
       DO 89 L = 1, N
    89 A(LI, L) = A(LI, L) - A(ICOL, L) *T
       IF (M) 135, 135, 18
    18 DO 88 L = 1, M
    88 B(LI, L) = B(LI, L) - B(ICOL, L) *T
   135 CONTINUE
C      FOLLOWING 11 STATEMENTS TO INTERCHANGE COLUMNS
   222 DO 3 I = 1, N
       L = N - I + 1
       IF (INDEX(L, 1) - INDEX(L, 2)) 19, 3, 19
    19 JROW = INDEX(L, 1)
       JCOL = INDEX(L,2)
       DO 549 K = 1, N
       T = A(K, JROW)
       A(K, JROW) = A(K, JCOL)
       A(K, JCOL) = T
   549 CONTINUE
     3 CONTINUE
    81 RETURN
       END
C      ***********************************************************
C      *                                                         *
C      *              GOLDEN SECTION OPTIMIZATION                *
C      *                                                         *
C      ***********************************************************
       FUNCTION FMIN(AX,BX,TOL)
       COMMON /BK1/ T(200),RT(200),RMT(200),PP(200),DTAB,TF,ND
       COMMON /BK2/ FOB,RJ,RNS
       COMMON /BK3/ RKS(200),PE,RA
       COMMON /BK4/ COEF(5),SDY,EDYAV,SDYAV,XMEDY,MP1
C
C      THE INTERVAL (AX,BX) IS DETERMINED.
C
C      AX LEFT POINT OF INITIAL
C      BX RIGHT POINT OF INITIAL
C
C      C IS THE SQUARED INVERSE OF THE GOLDEN RATIO
C
       QQQQ = 5.0000
       C = 0.5*(3.-SQRT(QQQQ))
C
C      EPS IS APPROXIMATELY THE SQUARE ROOT OF THE RELATIVE MACHINE
C      PRECISION
C
       EPS = 1.00
10     EPS = EPS/2.00
       TOL1 = 1.0+EPS
       IF(TOL1.GT.1.00) GO TO 10
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SY

      EPS = SQRT(EPS)                                                    A
C                                                                        A
C     INITIALIZATION                                                     A
C                                                                        A
      A = AX                                                             A
      B = BX                                                             A
      V = A+C*(B-A)                                                      A
      W = V                                                              A
      X = V                                                              A
      E = 0.0                                                            A
      CALL DEV(X)                                                        A
 117  FORMAT(2X,'--CHECK--',3F10.5)                                      A
      FX = FOB                                                           A
      FV = FX                                                            A
      FW = FX                                                            A
C                                                                        A
C     MAIN LOOP STARTS HERE                                              A
C                                                                        A
20    XM = 0.5*(A+B)                                                     A
      TOL1 = EPS*ABS(X)+TOL/3.0                                          A
      TOL2 = 2.0*TOL1                                                    A
C                                                                        A
C    CHECK STOPPING CRITERION                                            A
C                                                                        A
  118 FORMAT(2X,'--CHECK2--',5F10.4)                                     A
      IF (ABS(X-XM) .LE. (TOL2-0.5*(B-A))) GO TO 90                      A
C                                                                        A
C    IS GOLDEN SECTION NECESSARY                                         A
C                                                                        A
      IF(ABS(E) .LE. TOL1) GO TO 40                                      A
C                                                                        A
C    FIT PARABOLA                                                        A
C                                                                        A
      R = (X-W)*(FX-FV)                                                  A
      Q = (X-V)*(FX-FW)                                                  A
      P = (X-V)*Q-(X-W)*R                                                A
      Q = 2.00*(Q-R)                                                     A
      IF (Q .GT. 0.0) P = -P                                             A
      Q = ABS(Q)                                                         A
      R = E                                                              A
      E = D                                                              A
C                                                                        A
C    IS PARABOLA ACCEPTABLE                                              A
C                                                                        A
30    IF(ABS(P) .GE. ABS(0.5*Q*R)) GO TO 40                              A
      IF(P .LE. Q*(A-X)) GO TO 40                                        A
      IF(P .GE. Q*(B-X)) GO TO 40                                        A
C                                                                        A
C    A PARABOLIC INTERPOLATION STEP                                      A
C                                                                        A
      D = P/Q                                                            A
      U = X+D                                                            A
C                                                                        A
C    F MUST NOT BE EVALUATED TOO CLOSE TO AX OR BX                       A
C                                                                        A
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SY

      IF ((U-A) .LT. TOL2) D = SIGN(TOL1,XM-X)
      IF ((B-U) .LT. TOL2) D = SIGN(TOL1,XM-X)
      GO TO 50
C
C     GOLDEN SECTION STEP
C
40    IF (X .GE. XM) E = A-X
      IF (X .LT. XM) E = B-X
      D = C*E
C
C     F MUST NOT BE EVALUATED TOO CLOSE TO  X
C
50    IF (ABS(D) .GE. TOL1) U = X+D
      IF (ABS(D) .LT. TOL1) U = X+SIGN(TOL1,D)
      CALL DEV(U)
      FU = FOB
C
C     UPDATE A,B,V,W,A AND X
C
      IF (FU .GT. FX) GO TO 60
      IF ( U .GE. X) A=X
      IF ( U .LT. X) B=X
      V = W
      FV = FW
      W = X
      FW = FX
      X = U
      FX = FU
      GO TO 20
60    IF (U.LT.X) A=U
      IF (U.GE.X) B=U
      IF (FU.LE.FW) GO TO 70
      IF (W.EQ.X) GO TO 70
      IF (FU.LE.FV) GO TO 80
      IF (V.EQ.X) GO TO 80
      IF (V.EQ.W) GO TO 90
      GO TO 20
70    V = W
      FV = FW
      U = W
      FW = FU
      GO TO 20
80    V = U
      FV = FU
      GO TO 20
C
C     END OF MAIN LOOP
C
90    FMIN = X
      RETURN
      END
C ***************************************************************************
C
C           THIS OBJECTIVE FUNCTIOB IS FOR BMIN OPTIMIZATION
C
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SY:

C                                                                          AR
C ***********************************************************************  AR
      FUNCTION F(X)                                                        AR
      COMMON /BK2/ FOB,RJ,RNS                                              AR
                        RJ  = X                                            AR
C                      ********************************                    AR
C                      *                              *                    AR
C                      *  SPECIFY TT RANGE(AOP<SOP)   *                    AR
C                      *                              *                    AR
C                      ********************************                    AR
                        AOP =   0.0000001                                  AR
                        SOP =   0.0000001                                  AR
                        TOL = 1.0E-5                                       AR
                       RNS = FMIN(AOP,SOP,TOL)                             AR
                        F = FOB                                            AR
       RETURN                                                              AR
       END                                                                 AR
C   ***********************************************************************  AR
C                                                                          AR
C     GOLDEN SECTION SEARCH OF THE MINIMUM VALUE OF THE OBJECTIVE          AR
C     FUNCTION  FOR BETAC                                                  AR
C                                                                          AR
C   ***********************************************************************  AR
      FUNCTION BMIN(AX,BX,TOL)                                             AR
      COMMON /BK2/ FOB,RJ,RNS                                              AR
C                                                                          AR
C     THE INTERVAL (AX,BX) IS DETERMINED.                                  AR
C                                                                          AR
C     AX LEFT POINT OF INITIAL                                             AR
C     BX RIGHT POINT OF INITIAL                                            AR
C                                                                          AR
C     C IS THE SQUARED INVERSE OF THE GOLDEN RATIO                         AR
C                                                                          AR
      QQQQ = 5.0000                                                        AR
      C = 0.5*(3.-SQRT(QQQQ))                                              AR
C                                                                          AR
C     EPS IS APPROXIMATELY THE SQUARE ROOT OF THE RELATIVE MACHINE         AR
C     PRECISION                                                            AR
C                                                                          AR
      EPS = 1.00                                                           AR
10    EPS = EPS/2.00                                                       AR
      TOL1 = 1.0+EPS                                                       AR
      IF(TOL1.GT.1.00) GO TO 10                                            AR
      EPS = SQRT(EPS)                                                      AR
C                                                                          AR
C     INITIALIZATION                                                       AR
C                                                                          AR
      A = AX                                                               AR
      B = BX                                                               AR
      V = A+C*(B-A)                                                        AR
      W = V                                                                AR
      X = V                                                                AR
      E = 0.0                                                              AR
      FX = F(X)                                                            AR
      FV = FX                                                              AR
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

      FW = FX                                                           AR
C                                                                       AR
C     MAIN LOOP STARTS HERE                                             AR
C                                                                       AR
20    XM = 0.5*(A+B)                                                    AR
      TOL1 = EPS*ABS(X)+TOL/3.0                                         AR
      TOL2 = 2.0*TOL1                                                   AR
C                                                                       AR
C     CHECK STOPPING CRITERION                                          AR
C                                                                       AR
      IF (ABS(X-XM) .LE. (TOL2-0.5*(B-A))) GO TO 90                     AR
C                                                                       AR
C     IS GOLDEN SECTION NECESSARY                                       AR
C                                                                       AR
      IF(ABS(E) .LE. TOL1) GO TO 40                                     AR
C                                                                       AR
C     FIT PARABOLA                                                      AR
C                                                                       AR
      R = (X-W)*(FX-FV)                                                 AR
      Q = (X-V)*(FX-FW)                                                 AR
      P = (X-V)*Q-(X-W)*R                                               AR
      Q = 2.00*(Q-R)                                                    AR
      IF (Q .GT. 0.0) P = -P                                            AR
      Q = ABS(Q)                                                        AR
      R = E                                                             AR
      E = D                                                             AR
C                                                                       AR
C     IS PARABOLA ACCEPTABLE                                            AR
C                                                                       AR
30    IF(ABS(P) .GE. ABS(0.5*Q*R)) GO TO 40                             AR
      IF(P .LE. Q*(A-X)) GO TO 40                                       AR
      IF(P .GE. Q*(B-X)) GO TO 40                                       AR
C                                                                       AR
C     A PARABOLIC INTERPOLATION STEP                                    AR
C                                                                       AR
      D = P/Q                                                           AR
      U = X+D                                                           AR
C                                                                       AR
C     F MUST NOT BE EVALUATED TOO CLOSE TO AX OR BX                     AR
C                                                                       AR
      IF ((U-A) .LT. TOL2) D = SIGN(TOL1,XM-X)                          AR
      IF ((B-U) .LT. TOL2) D = SIGN(TOL1,XM-X)                          AR
      GO TO 50                                                          AR
C                                                                       AR
C     GOLDEN SECTION STEP                                               AR
C                                                                       AR
40    IF (X .GE. XM) E = A-X                                            AR
      IF (X .LT. XM) E = B-X                                            AR
      D = C*E                                                           AR
C                                                                       AR
C     F MUST NOT BE EVALUATED TOO CLOSE TO  X                           AR
C                                                                       AR
50    IF (ABS(D) .GE. TOL1) U = X+D                                     AR
      IF (ABS(D) .LT. TOL1) U = X+SIGN(TOL1,D)                          AR
      FU = F(U)                                                         AR
```

```
FILE: ARC2     FORTRAN  A                    VM/SP CONVERSATIONAL MONITOR SYS

C                                                                       AR
C                                                                       AR
      IF (FU .GT. FX) GO TO 60                                          AR
      IF ( U .GE. X) A=X                                                AR
      IF ( U .LT. X) B=X                                                AR
      V = W                                                             AR
      FV = FW                                                           AR
      W = X                                                             AR
      FW = FX                                                           AR
      X = U                                                             AR
      FX = FU                                                           AR
      GO TO 20                                                          AR
60    IF (U.LT.X) A=U                                                   AR
      IF (U.GE.X) B=U                                                   AR
      IF (FU.LE.FW) GO TO 70                                            AR
      IF (W.EQ.X) GO TO 70                                              AR
      IF (FU.LE.FV) GO TO 80                                            AR
      IF (V.EQ.X) GO TO 80                                              AR
      IF (V.EQ.W) GO TO 80                                              AR
      GO TO 20                                                          AR
70    V = W                                                             AR
      FV = FW                                                           AR
      U = W                                                             AR
      FW = FU                                                           AR
      GO TO 20                                                          AR
80    V = U                                                             AR
      FV = FU                                                           AR
      GO TO 20                                                          AR
C                                                                       AR
C     END OF MAIN LOOP                                                  AR
C                                                                       AR
90    BMIN = X                                                          AR
      RETURN                                                            AR
      END                                                               AR
```

```
   FILE: ARC2      DATA      A                VM/SP CONVERSATIONAL MONITOR SY
      ARC RUN NUMBER
    LIST          1020
      SAMPLE MASS
            1.517488
      BOMB MASS
            49.24316
      BOMB TYPE
                    5
      DATA TYPE
                    1
 1    START TEMPERATURE
              100.00
 2    END TEMPERATURE
              320.00
 3    SLOPE SENSITIVITY
               .0199
 4    HEAT STEP TEMP
               5.00
 5    DATA STEP TEMP
                .50
 6    CALC STEP TEMP
                .20
 7    BURST DIFFERENCE
              20.00
 8    COOL TEMP
              40.00
 9    RAD HEAT FRACTION
               1.00
10    PRESSURE RANGE
               2500
11    WAIT TIME
              30.00
12    ISO WAIT TIME
               500
13    ISOTH WINDOW
               2.00


5720.42   26.80   -.191
          12.2
STOP PLOT      10:11
 START UP
 84 APR 30     10:11
 ARC NO.            320
5720.88   26.77   -.191
          11.6
 HEAT          10:11
    .00 100.00    .611
          11.6
  WAIT         10:48
 30.00 101.03    .004
          11.5
SEARCH         11:18
```

```
FILE: ARC2      DATA      A                    VM/SP CONVERSATIONAL MONITOR SY

  40.10 101.06    .002
        11.5
 HEAT           11:29
  45.54 105.00    .370
        11.5
  WAIT          11:34
  75.54 105.41    .001
        11.6
SEARCH          12.04

    EXOTHERM
 84 MAY 01     04:12

 ARC NO.            320

   TIME    TEMP   RATE
         PRESS
1043.81 206.29    .024
        11.9
1067.36 206.89    .025
        11.8
1083.64 207.29    .024
        11.9
1107.10 207.89    .025    3
        11.9              3

END OF EXOTHERM
 84 MAY 01     07:42
 ARC NO.            320

   TEMP RISE   4.59
      CSUM        7.6

   4 ANALOG ERRORS
1254.11 210.89    .016
        11.9
 HEAT           07:43
1260.60 215.88    .278
        11.9
SEARCH          08:19


    EXOTHERM
 84 MAY 01     08:45

 ARC NO.            320

   TIME    TEMP   RATE
         PRESS
1316.39 217.25    .023
        11.9
1344.18 217.85    .021
        11.9
1360.64 218.25    .024
        11.9
```

```
FILE: ARC2      DATA      A                VM/SP CONVERSATIONAL MONITOR SYS

1387.41 218.85    .022
          11.9
1495.44 221.25    .026
          11.9
1568.18 223.25    .029
          11.9
1705.82 228.28    .045
          11.9
1796.78 233.26    .070
          11.9
1854.72 238.28    .111
          12.0
1881.58 243.31    .174
          11.9
1918.15 249.92    .288
          12.0
1928.77 253.82    .500
          12.0
1943.42 264.88   1.823
          12.0
1943.97 265.90   1.878
          12.0
1944.18 266.31   1.952    1
          12.0            1
1944.47 266.93   2.137
          12.0
1947.33 288.37  71.00
          12.0
1947.39 299.43 184.333
          12.0
1947.62 302.45   3.500    2
          12.0            2
1947.76 302.23  -1.571    3
          12.0            3
```

FILE: ARC2 RESULT A VM/SP CONVERSATIONAL MONITOR SYS

```
     ARC RUN NUMBER          =    320
     SAMPLE MASS             =      1.51749 GRAM

     BOMB MASS               =     49.24315 GRAM

     BOMB TYPE               =      5
START TEMPERATURE      =    100.0000
END TEMPERATURE        =    320.0000
SLOPE SENSITIVITY      =      0.0199
HEAT STEP TEMP         =      5.0000
DATA STEP TEMP         =      0.5000
CALC STEP TEMP         =      0.2000
BURST DIFFERENCE       =     20.0030
COOL TEMP              =     40.0000
RAD HEAT FRACTION      =      1.0000
PRESSURE RANGE         =      2.5000
WAIT TIME              =     30.0000
ISO WAIT TIME          =      0.6000
ISOTH WINDOW           =      2.0000
    EXOTHERM
 84 MAY 01    04:12
    EXOTHERM
 84 MAY 01    08:45
INITIAL TEMP.(K),TI                    =        490.400
RATE AT INITIAL TEMP.                  =          0.023
PRESSURE(PSIA) AT INITIAL TEMP.        =         11.900
MAX. SELF-HEAT RATE                    =        184.333
TEMP.(K) AT MAX. SELF-HEAT RATE        =        572.580
TIME (MINUTE) TO MAX. RATE             =        631.000
PRESSURE(PSIA) AT MAX. RATE            =         12.000
FINAL TEMP.(K)                         =        575.600
TEMPERATURE RISE,K                     =         85.200
MAXIMUM TEMPERATURE,K                  =        575.600
BOMB CORRECTION FACTOR,(PHI)           =          7.490
ADIABATIC RISE                         =         85.200
ADIABATIC RISE * PHI                   =        638.158
PRESSURE RATE AT INITIAL TEMP.         =          0.0
PRESSURE RATE AT MAX. RATE(PSIA/M)     =          0.0
HEAT OF REACTION                       =        484.196
HEAT CAP. AT CONS. VOL. OF SAMPLE      =          0.560
HEAT CAP. AT CONSTANT VOL.OF BOMB      =          0.100
```

YEXP(I) = ITH EXPERIMENTAL VALUE OF LN(RKS/T**RJ)
YC(I) = ITH CALCULATED VALUE OF LN(RKS/T**RJ) USING FITTED RN,RJ,RE AND
R = GAS CONSTANT, 1.987
RN = REACTION ORDER
RJ = TEMPERATURE FACTOR
RE = ACTIVATION ENERGY, CAL/MOLE
RA = FREQUENCY FACTOR
SDY = SUMMATION OF (YC(I) - YEXP(I)) FOR ALL I
EDYAV = AVERAGE ABS((YC(I)-YEXP(I))/YEXP(I))*100
SDYAV = AVERAGE ABS(YC(I)-YEXP(I))
XMEDY = MAX. ABS((YC(I)-YEXP(I))/YEXP(I))*100
DH = HEAT OF REACTION, CAL.

FILE: ARC2 RESULT A VM/SP CONVERSATIONAL MONITOR SY

SDY= 2.29 EDYAV= 0.530 SDYAV= 0.163 XMEDY= 1.018 DH

NUMBER OF DATA POINTS = 14
ACTIVATION ENERGY = 43751.863 CAL/MOLE
FREQUENCY FACTOR = 12.097
REACTION ORDER = 0.000
TEMPERATURE FACTOR = 3.931

DATA POINT NO.	TEMPERATURE	TIME	HEAT RATE	PRESSURE
1	490.400	1316.39	0.0230	11.900
2	491.000	1344.18	0.0210	11.900
3	491.400	1360.64	0.0240	11.900
4	492.900	1387.41	0.0220	11.900
5	494.400	1405.44	0.0260	11.900
6	496.400	1584.18	0.0290	11.900
7	501.410	1705.82	0.0450	11.900
8	506.410	1796.78	0.0700	11.900
9	511.430	1854.72	0.1110	12.000
10	516.460	1891.58	0.1740	11.900
11	523.070	1918.15	0.2880	12.000
12	526.970	1928.77	0.5000	12.000
13	536.030	1943.42	1.8230	12.000
14	539.050	1943.97	1.8780	12.000

T IS TEMPERATURE
YKT = YKS
YCT = CALCULATED VALUE OF YKS FROM FITTED COEFFICIENTS, THESE ARE RJ,RN
FREQUENCY FACTOR AND ACTIVATION ENERGY
RJ IS THETEMPERATURE FACTOR
RN IS THE REACTION ORDER
DYT = YCT - YKT
EDYT = DYT/YKT*100%
WHERE RKS = RMT*(DTAB/(TF-T))**RJ/DTAB
RMT IS THE TEMP RATE IN DEG. C/MIN.
TF IS THE FINAL (MAXIMUM) TEMPERATURE IN DEGREE K
T IS THE TEMPERATURE IN DEGREE K
DTAB = TF - INITIAL TEMPERATURE
= TEMPERATURE RISE IN DEGREE K

DATA NO.	T	YKT	YCT	DYT
1	490.3999	0.0003	0.0002	-0.0001
2	490.9998	0.0002	0.0002	-0.0000
3	491.3999	0.0003	0.0002	-0.0001
4	491.9998	0.0003	0.0002	-0.0000
5	494.3999	0.0003	0.0003	0.0000
6	496.3999	0.0003	0.0004	0.0000
7	501.4097	0.0005	0.0006	0.0001
8	506.4097	0.0008	0.0010	0.0002
9	511.4297	0.0013	0.0016	0.0003
10	516.4597	0.0020	0.0025	0.0004
11	523.0698	0.0034	0.0044	0.0011
12	526.9697	0.0059	0.0062	0.0004

```
FILE: ARC2      RESULT   A                    VM/SP CONVERSATIONAL MONITOR SY

        13        538.0298          0.0214          0.0160          -0.0054
        14        539.0498          0.0220          0.0174          -0.0046
        ND        RE        RA      RN        RJ      XMEDY    DH
        14    43733.594 12.054  0.00    3.93108     1.02   484.20
```